A Noniterative Model to Compute CO$_2$-H$_2$O Mutual Solubilities at 12–100°C and up to 600 Bar

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RESEARCH OBJECTIVES

Evaluating the feasibility of CO$_2$ geologic sequestration requires intensive numerical simulations of multiphase fluid flow. These simulations require the calculation of pressure-temperature-composition (P-T-X) data for mixtures of CO$_2$ and H$_2$O under moderate pressures and temperatures at which a CO$_2$-rich phase (gas or liquid) and an H$_2$O-rich liquid coexist. The objective of this study is to develop correlations to calculate efficiently and accurately the composition of these phases at equilibrium, for implementation into numerical simulations of water-CO$_2$ flows.

APPROACH

We compiled a large number of published experimental data on the mutual solubility of CO$_2$ and H$_2$O over our P-T range of interest into a database (403 data points). We then developed a solubility model, based on equating chemical potentials, and used a modified Redlich-Kwong (RK) equation of state to calculate fugacity coefficients for CO$_2$ and H$_2$O in the compressed gas phase. The mixing rules implemented in this model have a standard form but assume infinite H$_2$O dilution in the CO$_2$-rich phase. This allowed the use of a noniterative algorithm for computing mutual solubilities at given pressures and temperatures. RK parameters for pure CO$_2$ were obtained by fitting the equation of state to reference P-T data. Inverse modeling (PEST-ASP v5.0) was then used to calibrate the solubility model to the entire database of experimental P-T-X data, yielding RK parameters for the mixture, as well as aqueous solubility constants for gas and liquid CO$_2$ as functions of temperature and pressure. Water fugacities needed in the model were taken directly from literature sources.

ACCOMPLISHMENTS

A new model was developed to compute the mutual solubilities of CO$_2$ and H$_2$O at 12–100°C and up to 600 bar. The solubility model uses an efficient noniterative algorithm and reproduces experimental data typically within a few percent (Figure 1). The solubility model can be easily extended to moderately saline solutions, using existing activity coefficient models.

SIGNIFICANCE OF FINDINGS

Other CO$_2$-H$_2$O solubility models have been published in the literature. However, these models either do not cover our entire P-T range of interest or involve complex correlations
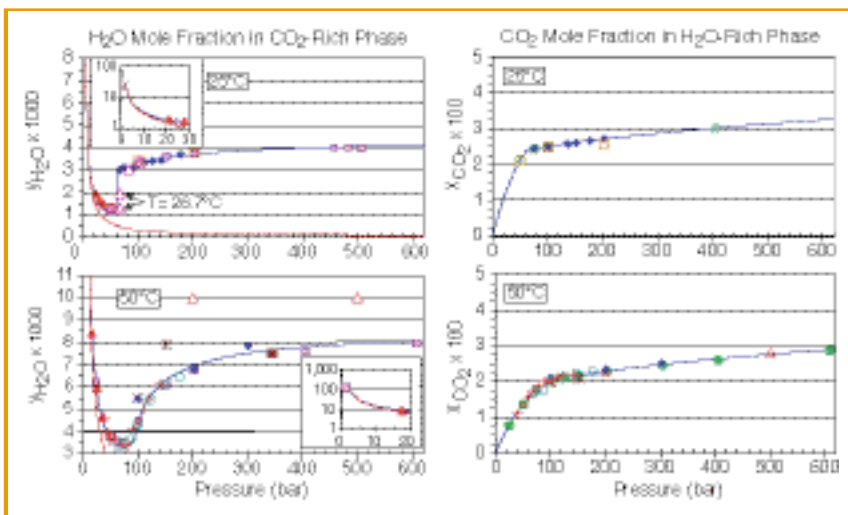

Figure 1. Calculated mutual solubilities of CO$_2$ and H$_2$O in this study (solid lines) and experimental data from the literature (symbols, with different shapes or colors for each different set of data). Dotted lines assume ideal mixing. Letters y and x refer to mole fractions in the compressed gas and aqueous phases, respectively.

requiring an iterative solution. Also, these models rely on a much smaller number of experimental data points. The noniterative procedure developed in this study reproduces experimental mutual solubilities of CO$_2$ and H$_2$O with sufficient accuracy for the study of geologic CO$_2$ disposal and enough simplicity to avoid degrading the performance of numerical fluid-flow simulations.

RELATED PUBLICATION

Spycher, N., K. Pruess, and J. Ennis-King, CO$_2$-H$_2$O mixtures in the geological sequestration of CO$_2$. I. Assessment and calculation of mutual solubilities from 12 to 100°C and up to 600 bar. Geochimica et Cosmochimica Acta, 2003 (in press); Berkeley Lab Report LBNL-50991, 2002.

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